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Anhydrous ethanol: A renewable source of energy

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ABSTRACT

Anhydrous ethanol is one of the biofuels produced today and it is a subset of renewable energy. It is considered to be an excellent alternative clean-burning fuel to gasoline. Anhydrous ethanol is commercially produced by either catalytic hydration of ethylene or fermentation of biomass. Any biological material that has sugar, starch or cellulose can be used as biomass for producing anhydrous ethanol. Since ethanol–water solution forms a minimum-boiling azeotrope of composition of 89.4 mol% ethanol and 10.6 mol% water at 78.2 °C and standard atmospheric pressure, the dilute ethanol–water solutions produced by fermentation process can be continuously rectified to give at best solutions containing 89.4 mol% ethanol at standard atmospheric pressure. Therefore, special process for removal of the remaining water is required for manufacture of anhydrous ethanol. Various processes for producing anhydrous ethanol have been used/suggested. These include: (i) chemical dehydration process, (ii) dehydration by vacuum distillation process, (iii) azeotropic distillation process, (iv) extractive distillation processes, (v) membrane processes, (vi) adsorption processes and (vii) diffusion distillation process. These processes of manufacturing anhydrous ethanol have been improved continuously due to the increasingly strict requirements for quantity and quality of this product. The literature available on these processes is reviewed. These processes are also compared on the basis of energy requirements.

Contents

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1. Introduction

Efforts are under way in many countries including India to search for alternatives of hydrocarbon-based fuels such as gasoline (petrol), diesel fuels, etc. The need for the alternative gasoline and diesel fuels arises mainly from the standpoint of preserving the global environment and the concern about long-term supplies of conventional hydrocarbon-based gasoline and diesel fuels. Among various alternatives, biofuels have been suggested as a blending component for gasoline and diesel fuels [1–5]. Anhydrous ethanol is one of the biofuels produced today. Other biofuels include biodiesel and biogas. Biofuels is a term used to describe raw biomass processed into a more convenient form to be used as a fuel. It is most commonly applied to liquid biofuels for transport but could also refer to gaseous fuels and solid such as wood pellets and briquettes. The use of biofuels enjoys benefits in the areas of environment, energy security and economic development. The use of biofuels instead of fossil fuels reduces net emissions of carbon dioxide, which are associated with global climate change. Biofuels are produced from renewable plant resources that recycle the carbon dioxide generated when biofuels are consumed. Biofuels also typically burn clearly in vehicle engines and reduce emissions of unwanted products, particularly unburned hydrocarbons and carbon monoxide. These characteristics contribute to improvements in local air quality. Biofuels help provide energy security for the countries that use them. Biofuels are produced from local and regional biomass resources and hence they are relatively isolated from the uncertainities of international political disruptions. Domestically produced biofuels also enhance national security by reducing net imports of petroleum and helping reduce international trade imbalances sometimes associated with oil imports. Biofuels create local and regional development opportunities; such developments frequently occur in rural areas where other options are very limited. The compatibility of biofuels with modern vehicles provides an option for replacing petroleum fuels in transportation. Current motor vehicles use technologies that permit a range of biofuel blends to be used for consumers. Most new vehicles today can readily accommodate biofuel blends up to about 20% and flexible fuel or dedicated fuel vehicles for high concentration blends or neat biofuels are also commercially available. As a result consumers have a variety of vehicle options available that will readily use biofuels.

Biofuels rely on biotechnology and are a subset of renewable energy [6]. Unlike other renewable energy forms, biofuels can be joined with production of chemicals, under the category called white biotechnology, as shown in Fig. 1.

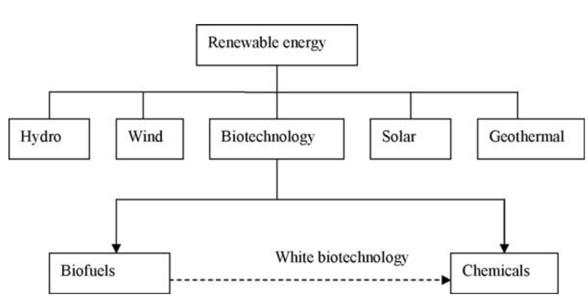


Fig. 1. Biofuels: a subset of renewable energy.

1.1. Anhydrous ethanol

Anhydrous ethanol, also known as absolute ethanol [7,8], is a clear, colourless and homogeneous liquid free from suspended matter and consisting of at least 99.5% ethanol by volume at 15.6 °C. The maximum water content, percent by volume at 15.6 °C, determined by Karl-Fisher method [IS:2362-1963] should be 0.5. The maximum specific gravity at 15.6 °C /15.6 °C should be 0.7961. Table 1 shows the requirements of anhydrous ethanol for use in automotive fuel in India [8]. The Indian standard IS:15464-2004 makes specific mention of a list of prohibited denaturants, which it states have extremely adverse effects on fuel stability, automotive engines and fuel systems. These materials may not be used in automotive fuels in any circumstances. They are as follows: methanol, pyrroles, turpentine, ketones and tars (high molecular weight pyrolysis products of fossil or non-fossil vegetable matter).

1.2. Raw materials for anhydrous ethanol

Ethanol is produced by fermentation of biomass [9–15]. Energy consumption is likely to increase appreciably in the coming years, mainly in densely populated countries like India, China and South Africa. To enable populous countries to achieve a standard of living similar to the industrial nations, all resources available on the globe have to be utilized. In order to reduce the carbon dioxide release to the atmosphere and meeting growing energy demands, ethanol is to be produced from feed stocks based on whole plant and biomass [16]. Ethanol can be produced from any biological material that has sugar, starch or cellulose [10]. Various steps involved in the conversion of biomass into anhydrous ethanol are the following:

1. Conversion of biomass into a useable fermentation feed stock (typically some form of sugar).
2. Fermentation of the biomass intermediates using biocatalysts (micro organisms including yeast and bacteria) to produce ethanol.
3. Processing of the fermentation product to yield anhydrous ethanol.

1.2.1. Sources of sugar

Ethanol can be produced from a large variety of carbohydrates (mono-, di-, polysaccharides). The most common disaccharides used for ethanol production is sucrose which comes from

Table 1
Indian specification of anhydrous ethanol for use in automotive fuel (IS:15464-2004) [8].

Characteristic	Requirement
1. Relative density @ 15.6/15.6 °C, max.	0.7961
2. Ethanol content @ 15.6 °C, vol.%, min. (excluding denaturant)	99.5
3. Miscibility with water	Miscible
4. Alkalinity	Nil
5. Acidity as acetic acid, mg/L, max.	30
6. Residue on evaporation, wt.%, max.	0.005
7. Aldehydes as CH_3CHO, mg/L, max.	60
8. Copper, mg/kg, max.	0.1
9. Conductivity, μS/m, max.	300
10. Methyl alcohol, mg/L, max.	300
11. Appearance	Clear and bright

sugarcane, sugar beet and sweet sorghum. The extracted sugarcane juice contains water (84%) and sugar (14%). The fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. Chemical reaction is composed of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars. First, invertase (an enzyme present in the yeast) catalyzes the hydrolysis of sucrose to convert it into glucose and fructose.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \overset{\text{invertase}}{\longrightarrow} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} \quad (1)$$

Then, another enzyme (zymase), also present in the yeast, converts the glucose and the fructose into ethanol and CO_2.

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \overset{\text{zymase}}{\longrightarrow} \underset{\text{Ethanol}}{2C_2H_5OH} + 2CO_2 \quad (2)$$

Monosaccharides (glyceraldehydes, xylose, ribose, glucose, fructose) consists of single sugars bound together with a general formula of $(CH_2O)_n$, where $n = 3–7$. The most common monosaccharides in nature are pentoses ($n = 5$, xylose) and hexoses ($n = 6$, glucose). One molecule of disaccharide results from a chemical reaction (dehydration synthesis) in which a new bond is formed between two monosaccharides after removal of water. Polysaccharides must be decomposed into disaccharides and/or monosaccharides through hydrolysis before fermentation.

1.2.2. Sources of starch

Grains (corn, wheat or barley) mainly provide starch. For example, corn contains 60–70% starch. Starch stored in grains is long chains of α-glucose monomers, 1000 or more monomers for one amylase molecule and 1000–6000 or more monomers for amylopectin. Polymers of α-glucose are broken into glucose through a hydrolysis reaction with gluco-amylase enzyme.

$$\underset{\text{Starch}}{(C_6H_{10}O_5)_n} + nH_2O \overset{\text{gluco-amylase}}{\longrightarrow} \underset{\text{D-glucose}}{nC_6H_{12}O_6} \quad (3)$$

The resulting sugar is known as dextrose or D-glucose that is an isomer of glucose. The enzymatic hydrolysis is then followed by fermentation, distillation and dehydration to yield anhydrous ethanol.

1.2.3. Sources of cellulose

Plants contain the cellulosic materials cellulose and hemicellulose. These complex polymers form the structure of plant stalks, leaves, trunks, branches and husks. They are also found in products made from plants, such as paper. Cellulosic feed stocks contain sugars within their cellulose and hemicellulose, but they are more difficult to biochemically convert into ethanol than sugar- and starch-based feed stocks. Cellulose resists being broken down into its component sugars. Hemicellulose is easier to break down, but the resulting sugars are difficult to ferment. The plant compound lignin also resists biochemical conversion. Significant progress has resulted in biochemical conversion processes to break down cellulose and hemicellulose and thermochemical conversion processes to break down lignin. Together, these processes could unlock the potential of cellulosic feed stocks for ethanol production.

Lignocellulose, which is the principal component of the plant cell walls, is mainly composed of cellulose (40–60% of the total dry weight), hemicellulose (20–40%) and lignin (10–25%). Cellulose molecules consist in long chains of β-glucose monomers gathered into micro-fibril bundles. The hemicelluloses can be xyloglucans or xylans depending on the types of plants. Backbone of the former consists of chains of β-glucose monomers to which chains of xylose (5-C sugar) are attached. The latter are mainly composed of xylose linked to a rabinose or/and other compounds that vary from one biomass source to the other. The hemicellulose molecules are linked to the micro-fibrils by hydrogen bonds. Lignins are phenolic compounds which are formed by polymerization of three types of monomers (p-coumaryl, coniferyl and synapyl alcohols). Lignin adds to the cell wall a compressive strength and stiffness. Cellulose is converted to simple sugars (monosaccharides), which are enzymatically hydrolyzed to yield ethanol under the following processes:

Dilute acid hydrolysis—Hydrolysis with a solution of sulfuric acid (0.5–1%) at about 160–190 °C for approximately 10 min occurs in two stages to maximize sugar yields from the hemicellulose and cellulose fractions of biomass. Liquid hydrolyzates are recovered from each stage, neutralized and fermented to ethanol. Dilute acid hydrolysis can be used to recover sugar from sugarcane bagasse.

Concentrated acid hydrolysis—This process is based on concentrated acid decrystallization of cellulose followed by dilute acid hydrolysis to sugars. Efforts are being made to commercially convert rice straw into ethanol and lignocellulosic components of municipal solid waste to ethanol.

Enzyme hydrolysis—Enzymatic hydrolysis of cellulose is achieved using cellulases, which are usually a mixture of groups of enzymes such as endoglucanases, exoglucanases and β-glucosidases acting in synergy for attacking the crystalline structure of the cellulose, removing cellobiose from the free chain ends and hydrolyzing cellobiose to produce glucose. Cellulases are produced by fungi, mainly *Trichoderma reesei*, besides *Aspergillus*, *Schisophyllum* and *Penicillium*. In order to reduce the cost of cellulase enzymes, simultaneous saccharification and fermentation (SSF) process for converting cellulose into ethanol has been introduced. In SSF process, cellulose, enzymes and fermenting microbes are combined, reducing the number of vessels and improving efficiency.

Cellulosic feed stocks suited to ethanol production include the following [5]:

- Agricultural residue—Crop residues such as wheat straw and corn stalks, leaves and husks.
- Forestry residue—Logging and mill residues such as wood chips, sawdust and pulping liquor.
- Grasses— Hardy, fast-growing grasses such as switchgrass grown specifically for ethanol production.
- Municipal and other wastes— plant-derived wastes such as household garbage, paper products, paper pulp and food-processing waste.
- Trees—fast-growing trees such as poplar and willow grown specifically for ethanol production.

These feed stocks have many advantages over sugar- and starch-based feed stocks. They are much more abundant and thus can be used to produce more substantial amounts of ethanol to meet gasoline demand. They are waste products or, in the case of trees and grasses grown specifically for ethanol production, can be grown on marginal lands not suitable for other crops. Less fossil fuel energy is required to grow/collect and convert them to ethanol and they are not human food products.

1.3. Uses of anhydrous ethanol

Anhydrous ethanol is used as chemical reagent, organic solvent, raw material for many important chemicals and intermediates for drugs, plastics, lacquers, polishes, plasticizers, cosmetics. It is also used in pharmaceutical formulations, production of biodiesel (fatty acid ethyl esters), electronic and military industries.

Anhydrous ethanol is considered to be an excellent alternative clean-burning fuel to gasoline [1–5]. In properly designed automotive systems, ethanol has the potential to achieve very low emission levels. In addition, the combustion products from renewable fuels such as ethanol are considered by many to be environmentally safe from a greenhouse standpoint [17]. It is reported that the ethanol content of solution for blending in gasoline should be 99.35% by volume to eliminate phase separation problems during distribution, storage and use. To make effective use of ethanol as a substitute fuel the energy consumed to make anhydrous ethanol must be less than the energy obtained from ethanol. The use of anhydrous ethanol as a transportation fuel in countries like Brazil, USA and India has been promoted. While the main consideration for Brazil and India has been to reduce dependence on oil imports, USA has been promoting ethanol to promote agriculture and also from environmental considerations. Blending of anhydrous ethanol in gasoline up to 20% is practiced in Brazil. In some areas of the United States, ethanol is blended with gasoline to form an E10 blend (10% ethanol and 90% gasoline), but it can be used in higher concentrations such as E85 or E95. Original equipment manufacturers produce flexible-fuel vehicles that can run on E85 or any other combination of ethanol and gasoline. Recently, Government of India has decided to enforce blending of 5 percent anhydrous ethanol in gasoline [18]. This decision will lead to: (a) reduction in petroleum import bill and (ii) conservation of indigenous petroleum reserves.

1.4. Comparison of properties of anhydrous ethanol and gasoline

Some of the properties [1,2,5,19–21] of the ethanol are compared with gasoline in Table 2. Ethanol has high octane number, which makes it an excellent gasoline blending component. The motor octane number is of particular significance because it characterizes the performance of a fuel in a hot engine under conditions of full load. The high octane number helps to run vehicles more smoothly and keeps a vehicle's fuel system clean for optimal performance. The heat of evaporation of ethanol is more than that for gasoline. Therefore, ethanol-fuelled engine may develop cold-start problems. The flame temperature for ethanol is lower than that for gasoline. Thus the combustion of ethanol will yield considerable reductions in NO_x emissions compared to gasoline. The oxides of nitrogen (NO_x) arises from nitrogen and oxygen in the air when at temperatures of 1093 °C and higher. Theoretically, the hottest flame comes from stoichiometric air/fuel mixtures, however, NO_x peaks at slightly leaner fuel/air ratios. Leaning of fuel/air ratio causes the flame temperature to be low enough to reduce NO_x as well as other emissions. Carbon monoxide emissions are almost entirely determined by fuel/air ratio. Ethanol unlike gasoline contains 35 wt.% oxygen so that less air is needed for combustion. Ethanol reduces carbon monoxide, volatile organic compounds, toxics and respirable-particulate emissions that pose a health hazard, particularly to children and seniors. On account of increased oxygen content in the fuel, the oxidation stability of the blended fuel could be slightly poor which may require use of higher dosage of additive to keep the engine clean. The increased NO_x emissions from four-stroke gasoline engines is another issue of concern as most of the studies indicate reduced CO and hydrocarbons but increased NO_x with ethanol blends. In the case of two-stroke engines, which do not emit NO_x, the use of ethanol–gasoline blends can result in substantial environmental benefits. The two-stroke engines in India from 2000 are also fitted with oxidation catalysts (catalytic converter). The studies indicate that strong potential of environmental improvement exists with use of ethanol–gasoline blends in the high population of two-stroke vehicles in Indian cities, particularly if they are retrofitted with oxidation catalyst while using the ethanol blended fuel [1]. The volumetric heating value of ethanol is less than that for gasoline. Per unit volume, ethanol has approximately 68% the energy of gasoline [5]. Ethanol has a lower Reid vapor pressure (RVP) than gasoline. A lower RVP makes cold-start ignition and operation of a spark-ignition engine difficult at low ambient temperatures. The possible solution of this problem is the on-board catalytic conversion of a portion of the ethanol fuel into diethyl ether and water [17]. Ethanol is quickly biodegradable in surface water, groundwater and soil. Since ethanol is a renewable fuel, it helps to reduce emissions of greenhouse gases that contribute to global warming. Ethanol helps to reduce pollution level.

Table 2
Fuel properties of gasoline and ethanol [1,2,5,19–21].

Characteristics	Gasoline	Ethanol
Chemistry	Mixture of hydrocarbons (C_5–C_{12})	C_2H_5OH
Specific gravity at 15.55 °C	0.72–0.75	0.79
Distillation temperature (°C)	32–210	78.4
Flash point (°C)	13	12
Kinematic viscosity (mm^2/s)	0.6	1.5
Reid vapor pressure at 37.8 °C (kPa)	35–60	17
Octane number		
(a) Research	91–100	111
(b) Motor	82–92	92
Oxygen content (wt.%)	0	34.7
Stoichiometric air/fuel ratio (w/w)	14.6	8.97
Net heat of combustion in		
(a) MJ/dm^3	32.2	21.2
(b) MJ/kg	43.5	27
Heat of vaporization in		
(a) MJ/dm^3	0.25	0.66
(b) kJ/kg	400	900
Water solubility	0	∞
Vapor flammability limits (vol.%)	0.6–8	3.5–15
Colour	Colourless to light amber glass	Colourless
Vapor toxicity	Moderate irritant	Toxic in large doses
Flame temperature at 101.325 kPa (°C)	392	478
Maximum flame speed (m/s)	0.40	0.33

Although anhydrous ethanol is completely miscible with gasoline at normal temperature, it is extracted by contact with small amounts of water, thus separating the blend into an upper gasoline-rich phase and a lower ethanol-rich phase. The separation can have highly undesirable effects. The lower phase is much greater in volume and lower in specific gravity than the original water and is more apt to be suspended and delivered to vehicles along with the upper fuel phase. The ethanol–water layer tends to pick up dirt or sediment; it can stall the engine upon reaching the carburetor and it is seriously corrosive to steel and to some metals commonly used for carburetor bodies and other fuel system parts. In addition, fuel in storage depleted of ethanol and lower phase with its high ethanol content would pose a disposal problem at distribution and marketing facilities. Most tanks in the commercial gasoline distribution system contain some water which would have to be rigorously excluded if gasoline in the system were to be replaced by ethanol–gasoline blends. The amount of water dissolved by gasoline–ethanol blend before breaking into two phases is dependent on the temperature, ethanol content and gasoline characteristics, particularly the aromatic content [2].

1.5. Demand and supply of anhydrous ethanol

Brazil is the largest single ethanol producer, followed by USA, China, India, France, Russia, South Africa and UK. Sixty percent of the world ethanol production is from sugar crops. India is the largest producer of sugar in the world and has high potential for

Table 3a
Ethanol availability based on production from molasses and its uses in India.

Year	Molasses production, ML	Production of ethanol, GL	Industrial use, ML	Potable use, ML	Other uses, ML	Surplus availability of ethanol, ML
1998–1999	7.00	1.41	534.4	584.0	55.2	238.2
1999–2000	8.02	1.65	518.9	622.7	57.6	454.8
2000–2001	8.33	1.69	529.3	635.1	58.8	462.7
2001–2002	8.77	1.77	539.8	647.8	59.9	527.7
2002–2003	9.23	1.87	550.5	660.7	61.0	597.5
2003–2004	9.73	1.97	578.0	693.7	70.0	627.5
2004–2005	10.24	2.07	606.9	728.3	73.5	665.8
2005–2006	10.79	2.19	619.0	746.5	77.2	744.3
2006–2007	11.36	2.30	631.4	765.2	81.0	822.8

ethanol production. The major source of ethanol production in Brazil and India and other sugar-raising countries is sugar–molasses route. In European countries, sugar beet is preferred. Sweet sorghum can be cultivated in temperate and tropical regions, increasing its potential benefits. Other crops that can yield oligosaccharides (potatoes, cereals, grapes, etc.) are generally not much utilized for bioethanol production with the exception of corn in USA. It is claimed that a variety of sweet sorghum has been developed with potential to produce 2–4 kL/ha/year of ethanol.

India produces nearly 1.3×10^9 L of ethanol utilizing less than half of its total installed capacity [1,22]. There are 295 alcohol distilleries in the country with an installed production capacity of 3.198×10^9 L. Ethanol is conventionally produced through fermentation processes from grains or other sugar bearing materials like sugarcane juice or molasses. Brazil produces most of its 11×10^9 L of ethanol from sugarcane. The USA produces ethanol mostly from corn starch. In India, molasses from sugar factories is the main source of ethanol production (Tables 3a and 3b). Ethanol can be produced from abundant sources of biomass, including agriculture and forestry residues, municipal solid waste, rotten grains, etc.

Table 3b
World ethanol production in 2006 (Thousand gallons).

Country	Production	Country	Production
European Union		South America	
Denmark	4.9	Argentina	44.9
France	251.0	Bolivia	18.5
Germany	202.2	Brazil	4,491.4
Hungary	17.2	Colombia	74.0
Italy	42.9	Ecuador	11.6
Poland	66.1	Other South America	50.2
Spain	122.5	Sub-total	4690.6
Sweden	30.4		
UK	74.0		
Other European Union	86.6		
Sub-total	897.8		
Europe			
Russia	171.7		
Turkey	17.2		
Ukraine	71.3		
Other Europe	65.6		
Sub-total	325.8		
Africa		Asia	
Egypt	7.9	China	1017.2
Kenya	4.5	India	502.0
Malawi	4.0	Indonesia	44.9
Nigeria	7.9	Japan	29.9
South Africa	102.4	South Korea	15.9
Swaziland	4.6	Pakistan	23.8
Zimbabwe	6.6	Philippines	22.2
Other Africa	22.2	Saudi Arabia	52.8
Sub-total	160.1	Thailand	93.3
		Other Asia	36.9
		Sub-total	1838.9
North/Central America		Oceania	
Canada	153.2	Australia	39.4
Costa Rica	10.6	New Zealand	4.2
Cuba	11.9	Other Oceania	2.1
Guatemala	21.1	Sub-total	45.7
Mexico	13.2		
USA	5276.9		
Other North/Central America	46.5		
Sub-total	5533.4		
		Grand total	13,492.3

2. Processes for production of anhydrous ethanol

Ethanol–water solution forms a minimum-boiling azeotrope of composition of 89.4 mol% ethanol and 10.6 mol% water at 78.2 °C and standard atmospheric pressure [23]. Ethanol boils at 78.4 °C, water boils at 100 °C, but the azeotrope boils at 78.2 °C, which is lower than either of its constituents. Indeed 78.2 °C is the minimum temperature at which ethanol–water solution can boil. When an azeotrope is partially boiled, the resulting vapor has the same ratio of constituents as the original mixture of liquids. Because composition is unchanged by partial boiling, azeotropes are also known as constant-boiling mixtures and further separation by conventional distillation is no longer possible. Hence, dilute ethanol–water solutions produced by fermentation process can be continuously rectified to give at best solutions containing 89.4 mol% ethanol at standard atmospheric pressure. Therefore, special process for removal of the remaining water is required for manufacture of anhydrous ethanol.

Various processes for producing anhydrous ethanol have been used/suggested. These processes of manufacturing anhydrous ethanol have been improved continuously due to the increasingly strict requirements for quantity and quality of this product. The various processes for the production of anhydrous ethanol are listed below:

1. Chemical dehydration process.
2. Dehydration by vacuum distillation process.
3. Azeotropic distillation process.
4. Extractive distillation processes.
5. Membrane processes.
6. Adsorption processes.
7. Diffusion distillation process.
8. Other processes.

The literature available on these processes is discussed below.

2.1. Chemical dehydration process

There are chemical dehydration processes that subject either ethanol liquors or ethanol vapors to the action of extremely hygroscopic substances forming fixed hydrates with water [4,24]. The principal substances employed for this purpose are quicklime, calcium chloride, potassium carbonate, etc.

The oldest method of producing anhydrous ethanol is the dehydration with quicklime. This process is still used on a laboratory scale. In this process, water is removed by a chemical reaction. Quicklime (calcium oxide) reacts with water to form calcium hydroxide. In this process, the ethanol–water solution is mixed with quicklime in a ratio of about 4.2 kg (or more) of lime for each kg of water to be removed (as determined with a hydrometer) and allowed to "slake" for 12–24 h with occasional stirring. The lime reacts with the water to form calcium hydroxide. The calcium hydroxide is insoluble in the ethanol and so the relatively pure (99.5 wt.%) ethanol goes to the top of the container and the calcium hydroxide settles to the bottom. The usual method of separating the lime and calcium hydroxide from the ethanol is by distillation. During distillation, the temperature should remain exactly at the boiling point of pure ethanol. Alternatively, but less desirable, the ethanol can be carefully drawn off (decanted) and filtered to remove any suspended particles that gives it a milky appearance. The calcium hydroxide may be converted back into calcium oxide and re-used. However, the temperatures required are quite high unless a vacuum drying oven is used. Although lime is relatively cheap and this process can produce a very high quality of anhydrous ethanol, but it is a batch process with a recovery of 97–98% and is expensive due to high energy inputs required. Therefore, this process has been suppressed.

2.2. Dehydration by vacuum distillation process

Vacuum distillation can be used for the production of anhydrous ethanol from aqueous ethanol. It is known that the concentration of ethanol in the ethanol–water azeotrope varies as the pressure changes [25]. The concentration of ethanol in the ethanol–water azeotrope increases with decrease in pressure. Below about 11.5 kPa, ethanol and water do not form an azeotrope and theoretically the components can be separated by conventional distillation. Such a separation at low pressure could involve a two-column arrangement: the first, to concentrate the ethanol at moderate pressure to the near azeotropic composition, and the second, to dehydrate the near-azeotropic mixture by distillation at low pressure (below about 11.5 kPa). The drawback of this operation is that it requires condensation temperature of 24.5 °C at 70 torr. High pressure operation also breaks the azeotrope but it leads to thermal decomposition. Black [26] presented calculations for low-pressure distillation column consisting of 60 trays and concluded that the production of anhydrous ethanol is not practical because this requires numerous trays and high reflux ratio, large diameter of the column and excessive requirement of steam.

2.3. Azeotropic distillation process

Azeotropic distillation is a widely practiced process for the separation of binary azeotropic mixtures into their pure component constituents. A classic example of azeotropic distillation is the production of anhydrous ethanol [27]. To produce anhydrous ethanol, the distillation equilibrium must be altered by the addition of third chemical component. The added component being present in the liquid phase can alter the activity coefficient of the various components and unless the components already present are identical in the physical and chemical properties, the change in activity coefficient will be different for each component, thereby altering their relative volatility. This technique is effective only when the component in the original mixture do not obey Raoult's law. In general, deviation from Raoult's law makes it easier to alter the relative volatility significantly by the addition of another component. Azeotropic distillation obeys this technique of adding a component to modify the relative volatilities. In this process, the volatility of the added component is same as that of the other components. It therefore forms an azeotrope with one or more of them due to difference in the polarity [28]. When the additional chemical species is usually selected so as to form azeotropes with more than one component in the feed, it is referred to as an entrainer. The added entrainer should be recovered by distillation, decantation, or another separation method and is returned to suitable position in the column. The quantity of lost entrainer is continuously fed to the system as make-up entrainer. The entire system is called azeotropic distillation [23].

Fig. 2 shows a flow diagram for separating water from ethanol, using benzene as the entrainer [23]. Ethanol is concentrated in a conventional distillation column to near the binary azeotropic composition. The concentrated ethanol is fed into the azeotropic column. A secondary feed, which is rich in entrainer, is introduced on the top tray. The bottom product from this tower is nearly pure ethanol. The overhead approaches the composition of ternary azeotrope and is fed into a decanter. The entrainer rich organic phase of the decanter and a small entrainer make-up stream comprise the secondary feed and is recycled to the azeotropic column. The aqueous phase of decanter is processed in one or more strippers to recover ethanol and entrainer. Various entrainers have been used in the azeotropic distillation to produce anhydrous ethanol [23,26–33].

For the production of anhydrous ethanol from dilute ethanol–water mixture, entrainer for azeotropic distillation is to be selected on the basis of the solubility parameter (δ) between 15 and 20 $MPa^{1/2}$ [29]. The δ value of ethanol is around 26 $MPa^{1/2}$ and that of water is around 47.8 $MPa^{1/2}$. A value of δ far from water and closer to ethanol will be selective to ethanol and will likely cause a phase split. Several compounds such as benzene [23,27], n-pentane [23,26], cyclohexane [28], hexane [29], n-heptane [30], isooctane [31,32], acetone [31], diethyl ether [26], polymers [33] can be used as an entrainer to produce anhydrous ethanol. Of these, benzene and cyclohexane have been used most extensively. Presently, benzene is in disuse due to its carcinogenic nature, although it is still being employed in some countries. The process using n-pentane is to be operated under high pressure because of low-boiling point of pentane.

Anhydrous ethanol from a mixture of ethanol and water using benzene was prepared by Young [27]. This process requires quite a lot of energy because it is necessary to maintain and recirculate large quantities of entrainer throughout the column to achieve the desired effect. In addition, pure ethanol must be adequately stored to prevent water from the atmosphere being absorbed by it. Instead of obtaining anhydrous ethanol, it is possible to directly attain a "dry" mixture of ethanol plus hydrocarbon, utilizing less

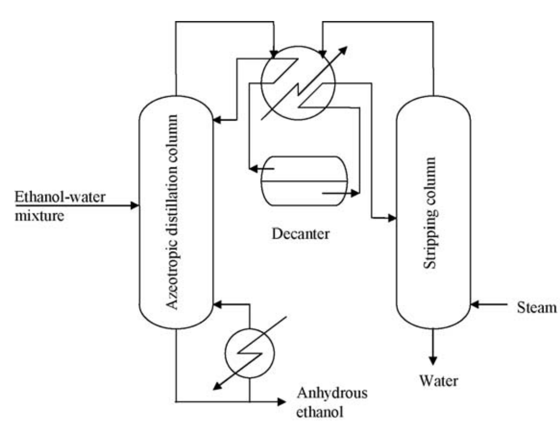


Fig. 2. Heterogeneous azeotropic distillation of ethanol–water mixtures.

energy. In this case, the high concentrations of entrainer necessary to circulate throughout the column are achieved by new input stream of the hydrocarbon and not by its vaporization–condensation. The ethanol plus hydrocarbon mixture thus obtained may be employed as an additive to gasoline without the need of subsequent distillation. Many of the constituents of gasoline may be used as entrainer in the dehydration of ethanol by azeotropic distillation. Experimental results have been obtained from a distillation column using a commercial mixture of isooctane with 11 components. Mixtures of these components of gasoline or some of the fractions used in refineries could be used to dehydrate ethanol instead of using purified components. Gomis et al. [31] studied the viability of an azeotropic distillation process using isooctane as an entrainer to dehydrate ethanol and obtain a mixture of ethanol plus isooctane without water experimentally as well as theoretically. The experimental results indicate that azeotropic distillation allows obtaining mixtures of isooctane plus ethanol with water concentrations lower than 50 ppm. The results indicate that the most critical parameter for this process is the reboiler heat duty. Low values of this parameter ($<$ 2.2 kJ/g of feed ethanol) produce mixtures of ethanol plus isooctane with excessive water contents. At high heat duty values ($>$3.6 kJ/g of feed ethanol) the azeotropic distillation column does not function properly, as the top stream condenses giving only one liquid phase.

High capital cost, high energy consumption, reliance on toxic chemicals like benzene and sensitivity to feedstock impurities are the disadvantages of the azeotropic distillation process. The anhydrous ethanol produced by this method is not used for medical purposes in Germany and France because of the use of toxic entrainer such as benzene.

2.4. Extractive distillation processes

2.4.1. Extractive distillation with liquid solvent

Extractive distillation with liquid solvent is used commercially for the production of anhydrous ethanol from ethanol–water mixtures. This method uses a relatively non-volatile liquid solvent which is fed into a distillation column some trays above the ethanol feed tray. The presence of the solvent at relatively high concentration in the liquid on the trays alters the volatility of one of the feed components more than the other, so a separation of the feed components can be made in the column. Such a solvent is referred to as an extractive distillation solvent. The solvent might be one which enhances the volatility of ethanol more than that of water. In this case, the ethanol would appear in the overhead product. Conversely, the solvent selected might enhance the volatility of water more than that of ethanol. In this case, water would appear in the overhead product. In either case, the solvent would appear in the bottom product and would normally have to be separated from the bottom product for recycle to the column for continuous operation. Fig. 3 shows a flow diagram of extractive distillation process for separating water from ethanol, using ethylene glycol as the solvent [23,24].

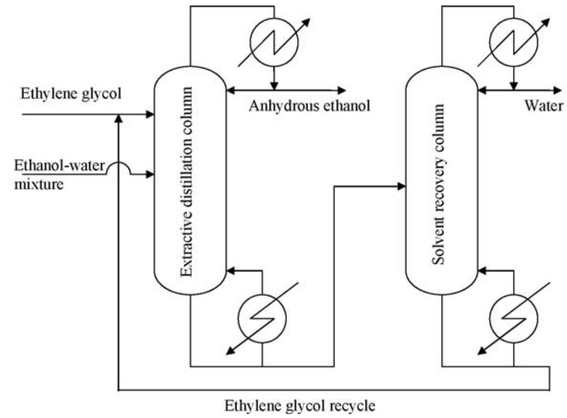


Fig. 3. Extractive distillation of ethanol–water mixture with ethylene glycol.

Several liquid solvents have been used to produce anhydrous ethanol [23,34,35]. These include ethylene glycol, diethyl ether, toluene and furfural. Extractive distillation with ethylene glycol as solvent [34] has features of high quality of product and suitability for large-scale production, relatively less volatilization amount and lower consumption of solvent. However, the solvent to feed ratio is too large, normally 5:1. Because of the large amount of recycling solvent, the additional consumption of energy is high. At the same time, the high liquid-phase load and low plate efficiency (20–40%) increase the number of plates and offset the effects of raising relative volatility and reducing the number of plates by introducing solvent to a great extent [36].

2.4.2. Extractive distillation with soluble salt

When a salt is dissolved in liquid solution consisting of two volatile miscible liquid components the salt may affect the activity of the two volatile components through the formation of liquid phase associations or complexes. If the dissolved salt associates preferentially with the molecules of one component of the liquid solution compared to those of the other, the solubility relationship between the two volatile components is altered such that one component is 'salted out' in respect to other. In such a case the activities of the two volatile components of the liquid solution are altered relative to each other in a manner which results in change of composition of the equilibrium vapor phase, despite the fact that no salt is present in the vapor phase. Hence, extractive distillation by use of a dissolved salt as separating agent can be applied to some systems, such as systems of low relative volatility or systems exhibiting azeotropic behavior in composition regions critical to separation, for which relatively small concentrations of salt are capable of increasing considerably the relative volatility of the more volatile component of the liquid solution to be distilled. This behavior, known as salt effect, is due to the preferential solvation of the ions (formed when the salt dissociates in solution) by the less volatile component of the liquid solution. In such a case, it is said that the more volatile component is salted out from the liquid to the vapor phase.

Extractive distillation with soluble salts is basically similar to extractive distillation with liquid solvents. The salt, a non-volatile component, is introduced at the top or near the top tray of the distillation column, flows downward along the column, and is completely removed with the bottom product. Compared to the extractive distillation with liquid solvents, the favourable aspects of extractive distillation with soluble salts are: (1) production of a distillate completely free from the salt (separation agent), (2) high level of energy savings due to the absence of the vaporization–condensation cycle of the volatile liquid solvent (separation agent) inside the column and (3) lower toxicity level of certain salts in comparison to previously cited liquids used in the production of anhydrous ethanol.

Several salts have been suggested for extractive distillation of ethanol–water system. Calcium chloride [37], cobalt (II) chloride [38], cupric chloride [39], nickel (II) chloride [39], strontium bromide [40], sodium and potassium acetates [41,42], calcium nitrate, sodium and potassium iodides [43], glucose [44], mercuric and lithium chlorides, mercuric and cupric chlorides [45] are among the most efficient salts. The use of salts to break the ethanol–water azeotrope for industrial production of anhydrous ethanol from dilute solutions dates back to the patents registered in the period 1932–1934 [46–49], which were the basis for the implementation of the HIAG process [50], licensed by DEGUSSA in

Germany [51,52]. It is reported that over 100 plants, with production capacities of up to 43,000 tonnes/year, based on that process, were built between 1930 and 1950 in Europe and elsewhere for the production of anhydrous ethanol (that was blended with gasoline to make gasohol containing 10% ethanol). The last of those plants ceased operation in 1965 in Brazil. The HIAG process employed a 70–30 molten mixture of potassium and sodium acetate (fed into the hot reflux stream of the distillation column) as agent to break the azeotrope, and produced anhydrous ethanol. The users of the HIAG process claimed lower capital and operating costs (energy consumption) in comparison with conventional azeotropic distillation using benzene or extractive distillation using ethylene glycol [50–52]. Considering such documented benefits, it is quite surprising that the HIAG process appears to be a neglected choice for the industrial production of anhydrous ethanol at the present time. Although some industrial plants have been used for the production of anhydrous ethanol from aqueous solutions, this process was never really successful because of the technical problems encountered in the handling of solid salts, in the dissolution and the subsequent recrystallization of the salt [53] and because of the need for special construction materials to avoid corrosion problems. On the other hand, at that time energy saving was not such a priority so as to encourage researchers to work on these problems.

Various methods have been suggested for the prediction and correlation of the salt effect on VLE in mixed solvent–salt systems. The most popular method for the correlation of salt effect data have probably been the equation proposed by Johnson and Furter [54]. For a single salt–binary solvent system at constant solvent composition, this equation expresses the variation of the relative volatility with salt concentration as:

$$\ln\left(\frac{\alpha_s}{\alpha}\right) = k_s x_s \tag{4}$$

where α_s and α are relative volatilities with and without salt, x_s is the mole fraction of salt and k_s is a salt effect parameter. For many systems, the salt effect parameter k_s can be regarded as independent of solvent composition. An empirical method for prediction of the salt effect on VLE was proposed by Lu [55]. Based on information on vapor pressure depression by the salt on each solvent, modified mole fractions are defined and used together with salt-free activity coefficients for prediction. For another predictive method proposed by Schmidt and Vogelpohl [56], three types of data are required: (1) salt solubilities in each solvent as a function of temperature, (2) solvent activities in each binary salt solvent system and (3) salt-free activity coefficients for the binary solvent mixture. The calculations are based on the assumption that the salt in the liquid mixture complexes with the solvent components in proportion to the solubility of salt in the pure solvents. A 'special binary approach' has been applied by Jaques and Furter [57,58] and by Rousseau et al. [59] for the calculation of the salt effect on VLE in salt-saturated systems. In this procedure the vapor phase fugacity of solvent n is calculated as:

$$\hat{f}_n^{v} = x'_n \gamma_n^{\text{pseudo}} (p_n^{\text{sat}} - \Delta P_n) \tag{5}$$

where x'_n is the salt-free mole fraction, γ_n^{pseudo} is a 'pseudo' activity coefficient, P_n^{sat} is the vapor pressure of pure solvent n and ΔP_n is the vapor pressure depression of solvent n by the salt at saturation. This means that the activity coefficients are normalized with respect to each salt-saturated solvent. These activity coefficients can now be correlated with one of the well-known local composition equations, such as the Wilson, or NRTL equation. A related method is 'pseudo binary approach' by Boone et al. [60] and Rousseau and Boone [61]. In this method solvent 1 plus salt is defined as component 1 and solvent 2 is defined as component 2. At constant solvent 1/salt mole ratio this defines a 'pseudo binary' system. The activity coefficients which arise from this procedure are described by the Wilson equation and the UNIQUAC equation. A major drawback of this correlation method is that at increasing concentrations of solvent 2 the salt concentration decreases, approaching zero for pure solvent 2.

Several methods based on excess Gibbs function have been proposed for prediction and correlation of salt effects on VLE [62–65]. The Margules equation has been used as the model for the excess Gibbs function. A ternary mixture of one salt in a binary solvent mixture requires one ternary and six binary parameters for calculation of the salt effect on VLE at constant temperature. The NRTL equation has been applied by Bekerman and Tassios [62]. Hala [63] combines the Margules equation with an empirical term which takes the electrostatic interaction between the ions into account. The model proposed by Sander et al. [65] combines a term of the Debye–Huckel type with a modified UNIQUAC equation with concentration dependent parameters. The model parameters are ion-specific and no ternary parameters are required. Applications of the model to ethanol–water–salt systems have been described.

Cook and Furter [53] describe the separation of ethanol–water mixtures in the presence of potassium acetate in a column with 12 bubble-cap trays. The salt was dissolved in the reflux and, after passing through the column, accumulated in the bottom. The measured concentration profiles along the column show oscillating ethanol fractions on the trays, indicating a non-stationary operation of the still. Some time later, Schmitt and Vogelpohl [66] demonstrated the feasibility of the elimination of the ethanol–water azeotrope using potassium acetate for a continuous pilot-plant sieve-plate column, and studied the effect of salt concentration and reflux ratio on the operation of the column.

Several innovative process flow sheets for the production of anhydrous ethanol have been proposed [67–69]. A process flow sheet, to produce anhydrous ethanol from dilute ethanol–water solutions, optimized for heat integration, and consisting of a preconcentration column (with intermediate heat pumps and optimal side-stream return), a saline extractive distillation column (using potassium acetate as separating agent), a salt-concentrating evaporator, and a spray dryer, was proposed and described in detail by Lynd and Grethlein [67]. Such a process was shown to involve lower capital costs and substantial energy savings as compared with conventional separation schemes used to make anhydrous ethanol. The use of calcium chloride to remove the ethanol–water azeotrope was experimentally shown and evaluated by Barba et al. [68] in a packed column. They reported a flow sheet of the process for industrial production of anhydrous ethanol, consisting of a preconcentration column, a saline extractive distillation column operated at subatmospheric pressure (0.25 atm), a vacuum evaporative crystallizer and a spray dryer; the latter two of these process units being needed for recovery of the anhydrous salt. The overhead vapor of the preconcentration column is fed to the dehydration column. They also made a theoretical evaluation of the dehydration process using calcium chloride, by simulating a mathematical model of the column about which they only reported the formal matrix structure of the equations. The set of experimental VLE data for the ethanol–water–calcium chloride system at 1 atm, reported by Nishi [70], was used to find the values of the parameters for their activity coefficient model, and those values were, therefore, used to simulate the dehydration column operated at 0.25 atm. Since the ethanol–water azeotrope can be eliminated by the sole cause of lowering the pressure to 0.11 atm, according to Black [26], then the production of anhydrous ethanol by saline extractive distillation at 0.25 atm is not due entirely to the salting out effect of calcium chloride. A procedure for the production of anhydrous ethanol using calcium chloride as separating agent was devised and

patented by Zeitsch [69]. The proposed process flow sheet consists of a steam-stripping preconcentration column operated at atmospheric pressure, a saline extractive distillation (or dehydration) column operated at subatmospheric pressure (0.34 atm), a two-stage vacuum evaporator, a spray tower, and a drum dryer; the latter three of these process units being needed for recovery of the anhydrous salt. The overhead vapor of the preconcentration column is fed to the dehydration column whose reflux is ethanol saturated with calcium chloride.

Several simulation studies of extractive distillation process to produce anhydrous ethanol have been carried out [71–73]. Siklós et al. [71] simulated the saline extractive distillation of ethanol–water mixtures. Two salts at saturation were tested as separating agents: sodium chloride and potassium acetate. For the calculation of VLE, the salt-containing liquid mixture was treated as a pseudo-binary system, and either the Wilson equation or an empirical correlation was used for estimating the equilibrium ratios of the pseudo-components ethanol and water. A simultaneous correction procedure based on the Newton–Raphson method was implemented by those authors to solve their model for the mole fraction and temperature profiles corresponding to the salt-containing system. The results obtained with the use of salt were compared with those of the salt-free system. A simulation study of saline extractive distillation columns for the production of anhydrous ethanol at atmospheric pressure was made by Cespedes and Ravagnani [72]. Three salts were tested as separating agents: lithium chloride, calcium chloride and potassium acetate. For the calculation of the material and energy balances, and the VLE behavior, the salt-containing liquid mixture was treated as a pseudo-binary system, and the UNIQUAC-E model by Sander et al. [65] was used for the calculation of activity coefficients for the pseudo-components ethanol and water. No validation of the predicted phase equilibrium behavior was made by Cespedes and Ravagnani [72]. Their model ignores the contribution of the salt to the energy balances, and a simultaneous correction procedure based on the Newton–Raphson method was implemented to solve the model for the mole fraction profiles of ethanol and the salt. Among the three salts considered, calcium chloride provides the largest salting out effect on ethanol and allows the use of a minimum number of separation stages. A simulation study of both conventional (using ethylene glycol) and saline extractive distillation for ethanol purification was carried out by Pinto et al. [73] with the help of a commercial process simulation package. Four salts were tested as separating agents: sodium chloride, potassium chloride, potassium iodide, calcium chloride. The main set of input data, specified parameters, and output data (such as stage temperature and composition profiles) reported for the saline extractive distillation process, were given for the case in which sodium chloride is used as separating agent. According to the results so reported, sodium chloride was shown to be entirely capable of removing the ethanol–water azeotrope at 1 atm. Surprisingly, this turns out to be contrary to the experimental evidence given long time ago by Johnson and Furter [54] about the actual inability for sodium chloride to eliminate this azeotrope even at a high concentration, corresponding to saturation of the salt in the ethanol–water solution. The same inability had been shown to be exhibited by potassium chloride. In contrast, potassium iodide had been shown to be capable of eliminating the azeotrope, but only at saturation as indicated in a later paper by Meranda and Furter [43]. The inconsistency between the experimental evidence available for sodium chloride and the simulation results obtained by Pinto et al. [73] might be related to the use of values not entirely validated for the parameters of the activity coefficient model (NRTL-E) that was chosen by those authors to calculate VLE ratios. In spite of the unexpected results for sodium chloride, it was shown by Pinto et al. [73], in agreement with previous works, that calcium chloride provides the largest salting out effect on ethanol and that saline extractive distillation (using calcium chloride) has a lower energy consumption as compared with conventional extractive distillation (using ethylene glycol). A rigorous steady-state equilibrium-stage model of saline extractive distillation columns on the basis of normalized MESH equations is proposed to simulated saline extractive distillation column for the particular case of the production of anhydrous ethanol at atmospheric pressure using calcium chloride as separating agent [73]. The choice of calcium chloride is due to the fact that it provides the largest salting out effect on ethanol, and also because not only the required VLE data but also experimental data or published correlations for the calorimetric properties are available for the ternary system ethanol–water–calcium chloride or the binary system water–calcium chloride, respectively, in contrast to the ethanol–water–potassium acetate system for which only VLE data can be found in the open literature. To demonstrate the azeotrope-breaking capability of the salt effect on its own (without the help of a lowered pressure), an atmospheric pressure operation is chosen for the simulation of the column.

The production of anhydrous ethanol from ethanol–water mixtures through salt addition has been demonstrated in a continuously operated single sieve-plate-column including salt recycling. They presented the effect of salt (potassium acetate) concentration as well as reflux ratio on the production of anhydrous ethanol from aqueous ethanol based on the experimental data. Several studies [74–81] on extractive distillation with salt have been reported. Ligero and Ravagnani [74] showed that anhydrous ethanol can be obtained from a dilute aqueous solution of ethanol via extractive distillation with potassium acetate. They proposed two process flow sheets with salt recovery. In the first, dilute ethanol is directly fed to a salt extractive distillation column and, after that; the salt is recovered in a multiple-effect evaporator followed by a spray dryer. In the second, the concentrated ethanol from conventional distillation is fed to a salt extractive distillation column. In this case, salt is recovered in a single spray dryer. In both the processes the recovered salt is recycled for use in the extractive distillation column. Their results show that the second process is more interesting in terms of energy consumption than the first.

Comprehensive review of the literature related to the vapor–liquid equilibrium of salt systems and the salt extractive distillation was presented by Furter and Cook [82] and complemented by Meranda and Furter [83], Furter [84]. Cook and Furture [53] developed a technique for dissolving salt into the reflux stream of a semiworks-scale column, involving the use of fluidized bed principle to rapidly dissolve the salt using a potassium acetate concentration of only 0.06 mole fraction, they were successful in eliminating the ethanol–water azeotrope. In summary, it is seen that some extractive distillation processes employing salt effect use a dissolved salt (or salts) as the extractive agent, while others use a liquid extractive agent with a salt (or salts) added to it.

2.4.3. Extractive distillation with salt dissolved in liquid solvent

Extractive distillation with salt dissolved in liquid solvent combines the principle of salt effect and conventional extractive distillation method. The presence of salt in liquid solvent enhances relative volatility. The relative effect of specific kinds of salt obeys the Dybel static-electric theory about salt effect [85]. The salt effect gradually decreases in the order of $AlCl_3$, $CaCl_2$ and NaCl. The trend is the same in the order of $Al(NO_3)_3$, $Cu(NO_3)_2$ and KNO_3. Besides, the salt effect gradually decreases in the order of Ac^-, Cl^- and $NO_3{}^-$. The industrial requirements for salt selection include low cost, chemical stability, high dissolvability, minor apparatus corrosion, less poisoning.

The influence of salt added in solvent in extractive distillation has been reported [86,87]. The vapor–liquid equilibria of the

systems ethanol–water, ethanol–water–ethylene glycol and ethanol–water–ethylene glycol–calcium chloride at finite concentration and normal pressure were measured by Lei et al. [86]. The experimental results showed that ethylene glycol–calcium chloride was more effective than ethylene glycol for separating ethanol and water. Gil et al. [87] simulated and analyzed an extractive distillation process for azeotropic ethanol dehydration with ethylene glycol and calcium chloride mixture using AspenPlus® simulator version 11.1. For obtaining a distillate with at least 99.5 mol% ethanol they determined the solvent to feed ratio of 0.3, molar reflux ratio of 0.35, number of theoretical plates of 18, feed plate (12th), solvent stage 3, solvent feed temperature of 80 °C.

Compared with the conventional extractive distillation, the extractive distillation with salt in solvent requires the reduced amount of the solvent recycled, the reduced number of theoretical plates, the reduced energy consumption and reduced cost of equipment.

2.5. Membrane processes

Membrane processes are mass transfer unit operations utilized for separations of liquid and gas streams. Membrane is an ultrathin semipermeable barrier separating two fluids and allows the transport of certain species through the barrier from one fluid to the other. It is this permeability that gives the membrane its utility and potential to separate a variety of process streams. The most universally employed membranes are composed of organic polymers, but metal, ceramic, liquid and gas membranes are also used. In all membrane methods, the membrane separates the fluid passing through it into a permeate (that which passes through) and a retentate (that which is left behind). When the membrane is chosen so that it is more permeable to one constituent than the other, then the permeate will be richer in the first constituent than the retentate.

Hyperfiltration (reverse osmosis) [88–91], pervaporation and gas/ vapor permeation [90] have been proposed for producing anhydrous ethanol. Hyperfiltration membranes with the appropriate separation capabilities (primarily, water rejection in the presence of ethanol) are required. Mehta [89] performed a preliminary analysis of ethanol dehydration using a hypothetical hyperfiltration membrane. Leeper and Tsao [90] introduced two ways of hyperfiltration process in recovery and purification of ethanol when lignocellulose is used as feedstock. The use of hyperfiltration significantly reduces the energy requirements of ethanol recovery from low-concentration ethanol in a corn to ethanol plant. The use of hyperfiltration based upon hypothetical water-rejecting hyperfiltration membrane is suggested to dehydrate high concentration ethanol in a corn to ethanol plant. Data on the separation of ethanol from water with cellulose acetate membranes have been reported by Choudhary et al. [91]. Vapor permeation is another membrane method in which the constituents pass through the membrane entirely in the vapor phase.

Pervaporation [92,93] is a new generation of membrane separation process. This process involves a phase change and has the potential for the production of anhydrous ethanol from aqueous ethanol. During pervaporation, a liquid stream is separated on a semi-permeable membrane (for ethanol dehydration-hydrophilic laminated membranes) into two streams: a gaseous permeate and liquid retentate. A permeate is enriched with a component transmitted preferentially by the membrane opposite to the retentate which has a small amount of this compound. Since separation on the membrane does not much depend on liquid– vapor equilibrium (in the pervaporation transport of water is usually preferred), the process can be used efficiently for separating azeotropes and close boiling liquids. Pervaporation using hydrophilic membranes and vaporization of water offers an alternative process to produce anhydrous ethanol. A vacuum is created on one side of the membrane, with separation of ethanol and water determined by their differing diffusion resistances through the membrane and differences in partial pressures. Water permeates through the membrane, while dehydrated ethanol remains as the retentate. Several companies such as GFT, Kalsep and Lurgi have constructed membrane separation plants which utilize the pervaporation process or the vapor permeation process where flat membranes are used [93]. The size of such an apparatus is large, their operation ability is not good, and their efficiency is not necessarily high. Tsuyumoto et al. [93] performed pervaporation experiments in a pilot plant equipped with hollow-fiber membranes in a module form. They operated a plant equipped with modules of 6 m^2 effective membrane area to process ethanol (94 wt.%) –water (6 wt.%) mixture at a flow rate of 100 kg/h steadily for over two months and produced anhydrous ethanol with negligible loss of ethanol. In the sweeping gas pervaporation process used for dehydration of ethanol–water mixture, hollow fiber membrane having hydrophilic properties in contact with the mixture is used which resulted in increased separation factor. For commercial application, a suitable membrane with the development of the LURGI pervaporator consisting of a special plate type membrane and an integrated permeate condenser combined in one compact unit is used. It operates in dehydration of ethanol–water mixture. A tubular type membrane is prepared either on the inner or on the outer surface of a porous ceramic support with cellulose acetate by a dip-coating and rotation drying techniques for dehydration of ethanol. The overall mass transfer coefficient of water will depend upon feed flow rate. With the increase in feed temperature the mass transfer coefficient of water in ethanol increases. The ceramic support coated with cellulose acetate can be recovered by the solvent and sonication treatment. So dehydration of ethanol will be accomplished. The mechanism of ethanol–water separation by pervaporation has been studied by Mulder and Smolders [94], Mulder et al. [95]. Data have been reported for the separation of azeotropic ethanol–water mixtures by pervaporation using membranes made of blends of polyacrylonitrile and polyvinyl pyrrolidone [96]. Wenzlaff et al. [97] have characterized the performance of crosslinked styrene-butadiene membranes and cellulose triacetate. The separation of ethanol–water mixtures by pervaporation has been studied by the use of sulfonated polysulfone membrane [98], photopolymerised composite membrane [99], aromatic polyamide membrane [100], lithiated polysulfonate membrane [101], composite chitosan membrane [102]. The design and operation of pervaporation plant for ethanol dehydration has been presented by Sander and Soukup [103].

2.6. Adsorption processes

Adsorption processes employ molecular sieves that selectively adsorb water on the basis of the difference in molecular size between water and ethanol. A molecular sieve is a material containing tiny pores of a precise and uniform size. Synthetic zeolite in pellet form can be used, as well as a variety of plant-derived adsorbents, including cornmeal, straw, and sawdust. Often, it consists of aluminosilicate minerals or synthetic compounds that have open structures through which small molecules can diffuse, such as clays, porous glasses, micro porous charcoals, active carbons etc. Molecules small enough to pass through the pores are adsorbed while larger molecules are not. Ethanol dehydration is accomplished with molecular sieves which have a diameter of 3 Å, which entraps water molecules which have a diameter of 2.5 Å. Ethanol molecules which have a diameter of 4 Å cannot enter and therefore flow around the material. Molecular sieve can adsorb water up to 22% of its own weight. The zeolite bed

can be regenerated essentially an unlimited number of times by drying it with a blast of hot carbon dioxide. Cornmeal and other plant-derived adsorbents cannot readily be regenerated, but where ethanol is made from grain, they are often available at low cost. Absolute ethanol produced this way has no residual benzene.

The process of dehydration of ethanol can be understood as follows. Consider a column packed with freshly activated molecular sieve. As ethanol–water vapors first enter the bed, water is diffused and adsorbed within the pores of the adsorbent structure in a thin layer. As more ethanol enters the column, it passes through this layer to slightly lower level where another incremental amount of water is adsorbed. This continues until a point is reached where all possible water adsorption from ethanol solution is accomplished. Transfer of water from the vapor of ethanol–water solution to the molecular sieve occurs through a zone where water (adsorbate) content is reduced from its inlet to its outlet concentration. This finite length of bed, where the adsorbate transfer occurs, is known as the mass transfer zone. Two beds are provided in order to make the process continuous. While the active bed is under pressure carrying dehydration, the regeneration bed is under vacuum. The shift of operation (swing) from one bed to another is controlled with the help of control valves and automation.

Several studies have shown that it is possible to use biomaterials for ethanol dehydration. Ladisch et al. [104] used starch (corn and potato), xylan, pure cellulose and corn residue for the separation of ethanol–water mixture in the vapor phase. They concluded that these materials had the capacity of adsorbing water in the decreasing order: corn starch, corn residue, xylan and pure cellulose. They explained this fact due to concentration of amylopectin present in each studied material. The capacity of adsorption will be greater when the concentration of amylopectin is more. The use of starch products to adsorb water has been broadly studied to develop models for fitting experimental thermodynamic and kinetic data for this new adsorbent. A study on the adsorption of pure water vapor on starch using the air as a carrier gas has been reported and the isotherms show adsorption capacity of the order of 0.16 kg of water/kg of starch. The saturation of the bed occurs in about 2 h, with the adsorbed amount being directly proportional to the concentration of water in the air. The maximum diffusivity value obtained was of the order of 14×10^{-13} m^2/s. A thermodynamic and kinetic study of liquid phase adsorption of water from ethanol–water mixture using starch as the adsorbent has also been reported.

The regeneration in typical cyclic systems constitutes removal of the adsorbate from the molecular sieve bed by heating and purging with a carrier gas. Sufficient heat must be supplied to raise the temperature of the adsorbate, the adsorbent and the vessel to vaporize the liquid and offset the heat of wetting the molecular sieve surface. The bed temperature is critical in regeneration. Bed temperatures in the 175–260 °C range are usually employed for type 3 Å. This lower range minimizes polymerization of olefins on the molecular sieve surfaces when such materials are present in the gas. Slow heat up is recommended since most olefinic materials will be removed at minimum temperatures; 4 Å, 5 Å and 13× sieves require temperatures in the 200–315 °C range. After regeneration, a cooling period is necessary to reduce the molecular sieve temperature to within 15 °C of the temperature of the stream to be processed. This is most conveniently done by using the same gas stream as for heating, but with no heat input. For optimum regeneration, gas flow should be countercurrent to adsorption during the heat up cycle, and concurrent (relative to the process stream) during cooling. Alternatively, small quantities of molecular sieves may be dried in the absence of a purge gas by oven heating followed by slow cooling in a closed system, such as a desiccator. This method shows good dehydration effect and produces high quality product in batch wise manner. So, large-scale production of anhydrous ethanol cannot be done by this process.

The conventional means for regenerating the sieves is to desorb the adsorbed water with a stream of hot gas, typically at a temperature of 288 °C. This requires considerable energy since the entire system must be heated to a temperature at which water is desorbed. Furthermore, additional energy is required to maintain the system at the elevated temperature for the duration of desorption cycle, which typically lasts 2–4 h. A method for the regeneration of molecular sieves with methanol or acetone is proposed. This method provides a scheme for regeneration without the use of heat of molecular sieves and also permits the molecular sieves to be returned to dehydration service immediately after regeneration. The regeneration procedure can be conducted in either a batch or continuous manner. For example, in a typical batch regeneration procedure, spent molecular sieves to be regenerated are placed into a vessel and methanol or acetone preferably containing not more than 0.1% by weight water is brought into contact with the molecular sieves. The amount of methanol or acetone used generally ranges from about at least 2–10 mL for each gram of the molecular sieves undergoing regeneration. A large ratio of methanol or acetone to the molecular sieve, such as 10 or more to 1, milliliters per gram, is generally preferred to desorb the maximum amount of water. Occasional stirring or other agitation is desirable to improve regeneration efficiency. The methanol or acetone is permitted to remain in contact with the molecular sieves for periods of from about 0.1–24 h. The extent of water desorbed from the molecular sieves increases with extended contact times but with decreasing efficiency. A 24 h contact or equilibration period removes most of the water from the spent molecular sieves, but a 4-h equilibration period usually removes over 90% of the water removed in 24 h. Thus, from a practical standpoint, a 4-h equilibration or contact period is generally sufficient. After contact with the methanol or acetone for a desired period, the molecular sieves are separated from the bulk of the methanol or acetone by filtration or centrifugation. It is not necessary to treat the regenerated molecular sieves further and they can then be used for dehydration operations. So this method avoids placing stresses on the sieves resulting from high temperature regeneration and subsequent cooling cycles.

Activated carbon works as a hydrophobic adsorbent selective for ethanol over water and a unique means for recovering the ethanol which is particularly suited for the subsequent use of the extract stream in gasohol. To separate ethanol from a feed mixture containing ethanol and water, the mixture is contacted with the adsorbent and the ethanol is more selectively adsorbed and retained by the adsorbent while the water is relatively unadsorbed and is removed from the interstitial void spaces between the particles of adsorbent and the surface of the adsorbent. The adsorbent containing the ethanol is referred to as a "rich" adsorbent-rich in ethanol.

In a study, ethanol-rich vapors (80–92% ethanol) leaving a first stage distillation at a temperature of about 78–80 °C are passed directly onto a column of cornmeal to adsorb water and obtain anhydrous ethanol. After the column is saturated, the cornmeal is regenerated by passing hot (90–120 °C) air over it; simultaneously, a second previously regenerated column is brought into operation. Overall energy expenditure for the distillation and sorption processes including the distillation step is about 4187 kJ/kg. Disadvantages of this method are that regeneration of the cornmeal sorbent is required, ethanol adsorbed onto the cornmeal is not recovered, the sorption process must be physically connected to the distillation operation, and amyl acetate generated during the distillation process pass onto the column and may lead

to reduced efficiency. Furthermore, since the capacity of cornmeal to adsorb water decreases as the temperature is increased from ambient, efficiency of the sorbent is less at the temperature of the process than if the operation was carried out at lower temperatures.

The process of dehydration on molecular sieves can adsorb much water or other compounds and remove liquid and gaseous pollutants to very low concentrations (ppm or less). For ethanol dehydration on industrial scale, potassium and sodium zeolites are used [105]. Ethanol dehydration on molecular sieves is connected with cyclic work in changeable conditions, consumption of large amounts of vapor under high pressure and recycling large quantities of ethanol to the process.

In a study by Benson and George [106], a thermal swing adsorption column was used to evaluate the effectiveness of three lignocelluloses-based adsorbents (bleached wood pulp, oak sawdust and kenaf core) on the removal of water from ethanol–water mixtures of 90, 95 and 97 wt.% ethanol. They generated breakthrough curves to determine the effectiveness of these adsorbents and to compare these adsorbents with starch-based adsorbents. They observed that water is preferentially adsorbed allowing for complete dehydration of ethanol. They also presented the mass transport properties for the diffusion of water molecules into porous matrices of the adsorbents as well as the length and velocity of mass transfer zone.

A non-isothermal, non-adiabatic model has been developed for the bulk vapor phase adsorptive drying of ethanol–water azeotrope in short, small diameter columns [107]. This model incorporates an overall two-film linear mass transfer driving force, a variable axial velocity and a temperature dependent Langmuir isotherm. Breakthrough curves and temperature profiles generated by the model were compared with those obtained experimentally. The relative importance of each of the two film resistances is discussed for various periods during both adsorption and desorption.

2.7. Diffusion distillation process

A new separation process for azeotropic mixtures – diffusion distillation – is proposed by Fullarton and Schlunder [108,109]. In this process, a liquid is evaporated below the boiling temperature, diffuses through an inert gas gap and is recondensed. Hence the separation effect is not only based on the relative volatility of the components concerned but also on their diffusivity in the inert gas. A significant separation effect can be achieved in a wetted-wall column consisting of two concentric tubes. They carried out several experiments with a binary isopropanol–water mixture and a ternary isopropanol–water–methanol mixture at different evaporation and condensation temperatures, with different inert gases and annular widths in the wetted-wall column. They found that the experimental results were well described by the vapor–liquid equilibrium and the Stefan–Maxwell equations, that is, by steady-state molecular diffusion. They demonstrated the concept in terms of behavior at a single point in their diffusion distillation experiment and modeling, so their analysis did not completely describe the nature of the process nor did the results give an indication of the extent of separation. McDowell and Davis [110] extended the investigation and the description of process behavior to an integral column via computer simulation. The study exposes process parameters for diffusion distillation that are not evident from the differential analysis and provides insights into already established parameter. The model presented shows an improvement over the model of Fullarton and Schlunder. This process has been suggested for producing anhydrous ethanol by Taylor and Krishna [111]. Chung et al. [112] dehydrated ethanol by this method in wetted wall column and observed the effect on temperature difference between evaporation part and condensation part, effect of annular part and inert gas on selectivity and total flux. Kim et al. [113] developed a model for the above process in consideration of sensible heat transfer and developed an algorithm which enables to calculate interfacial temperature more precisely at condensing liquid film.

2.8. Other processes

Highly integrated recovery processes, such as multi-pressure, vapor recompression distillation are reported to reduce the energy requirements of ethanol purification greatly [114]. The combined use of distillation and pervaporation is also being studied [115,116]. In supercritical fluid extraction, carbon dioxide has been studied as the solvent used for the production of anhydrous ethanol [117]. The use of liquid CO_2 to extract the ethanol and then depressurizing it to flash off CO_2 is also used in recovering anhydrous ethanol. Indirect dehydration in which ethanol–gasoline blends are directly produced has been proposed. These processes include extractive distillation using gasoline as the entrainer [118] and liquid–liquid extraction using gasoline as solvent [119–121].

The differential miscibility of castor oil in ethanol and water can be exploited to separate ethanol from water. In this process castor oil is added to an ethanol–water solution. The ethanol mixes freely with castor oil, which is insoluble in water. The resulting ethanol–castor oil phase, which contains less than 1% water, can be collected as top layer, the bottom layer being the remainder of the ethanol–water solution somewhat depleted in ethanol. Heating this two-layer mixture to a temperature slightly below the boiling temperature of ethanol would cause the partial pressure of ethanol above the top layer to be much greater than the partial pressure of either castor oil or water. This vapor-phase ethanol can be condensed in a relatively pure state. This separation process could be exploited industrially to produce clean fuel from fermented ethanol. The differential solubility of sulfur in ethanol and water can be exploited to separate ethanol from water.

A method of dehydrating ethanol–water mixture is proposed in which a carrier gas is used to vaporize the solution and transport the vapors to a sorbent where water is sorbed in preference to ethanol. This method is particularly suited for small-scale production of anhydrous ethanol for blending with gasoline. In this method an ethanol–water solution is contacted with a carrier gas in a manner such that a portion of the solution is vaporized and the carrier gas becomes at least partially saturated with water and ethanol vapors. The so-saturated carrier gas is passed in the proximity of a sorbent which sorbs water vapor in preference to ethanol vapor so that the carrier gas subsequent to passing over the sorbent contains a ratio of ethanol to water which is greater than that prior to passing over the sorbent. The concentrated ethanol is collected. The circulation of the carrier gas during the contacting and passing steps is carried out without contact with the outside atmosphere. The primary advantage of this method over the azeotropic distillation method is the substantial reduction in energy spent. The energy consumed in this process is about 100 cal/g to produce 99.35% ethanol from 95% ethanol versus 498–783 cal/g for the industrial azeotropic process. In addition, capital outlay and maintenance costs for the sophisticated equipment required for azeotropic distillation are eliminated.

Ethanol also has several desirable characteristics for separation by chemical complexation [34]. Ethanol has a low activity coefficient in water, therefore, extraction with conventional solvents is difficult. Although ethanol is substantially more volatile than water in dilute solutions, it forms an azeotrope with water at high concentrations, making distillation processes complicated and possibly expensive. However, chemically complexing extrac-

tants have not been identified that provide high values of distribution coefficient for ethanol. Measurements have shown that amines and phosphoryl compounds do not provide values of distribution coefficient appreciably greater than those provided by conventional solvents. Alcohols have both Lewis-acid and Lewis-base sites. One possible explanation for low distribution coefficient values is that the association of hydroxyl groups with another in the aqueous phase is significant compared to the association with the extractant in the organic phase. Although solvents with high capacity have not been identified, complexation effects can improve the selectivity of potential solvents.

In the recovery of ethanol from aqueous solution, coextraction of water has a large effect on process economics. Solvents may be compared by plotting the selectivity (separation factor between ethanol and water) versus the solvent capacity of ethanol, expressed as distribution coefficient. Such a plot for extraction of ethanol from relatively dilute aqueous solution by many different solvents is given by Rousseau [34]. The Lewis-acid solvents (alcohols, carboxylic acids and chlorinated hydrocarbons) provide much better selectivity for a given capacity than do the Lewis-base solvents (ketones, esters, amines, phosphoryls). Furthermore, branching of the solvent molecule is important. Branched carboxylic acid gives substantially high selectivity than do straight-chain acids for a given value of distribution coefficient. The same is true for alcohols. Many investigation of the extraction of ethanol from water have postulated that a very high selectivity is needed to enrich the solvent-free extract to ethanol content near or above the binary azeotrope with water. However, this degree of enrichment is not necessary. The extraction step can be followed by an extractive-distillation dewatering step.

3. Energy requirements of anhydrous ethanol production

Anhydrous ethanol production requires energy for the preparation of useable fermentation feedstock, the fermentation of prepared feedstock and distillation/dehydration of dilute ethanol–water mixtures. The different sources of biomass have been compared on the basis of the net energy value (NEV) of ethanol, determined by subtracting the energy required to produce a liter of ethanol during the whole life cycle from the energy contained in a liter of ethanol. The NEV of ethanol from sugarcane, corn and cellulose is reported to be 11.39, 5.57–6.99, 17.65–18.93 MJ/m^3, respectively [122]. The energy consumed in the preparation of fermentation feedstock (typically some forms of sugar) varies in the range of 1.1–15 GJ/m^3 of anhydrous ethanol [90,122]. The processes for fermentation of prepared feedstock and production of anhydrous ethanol are similar regardless of the biomass. The fermentation step consumes very little energy.

The dilute ethanol–water mixture is usually first concentrated by fractional distillation to 92–94 wt.% ethanol and then is dehydrated by one of the several processes discussed earlier to produce anhydrous ethanol. The energy requirements of ethanol purification by fractional distillation remain essentially constant for feeds containing more than 15–20 wt.% ethanol and less than 92–94 wt.% ethanol. As ethanol concentration in the feed decreases, the reflux ratio required must increase dramatically and this results in an increased energy requirements. The fractional distillation requires a disproportionate increase in energy at product concentrations above 92–94 wt.% ethanol due to the shape of the vapor–liquid equilibrium curve for ethanol–water system which results from the formation of non-ideal ethanol–water solution, including the formation of an azeotrope at 95.57 wt.% ethanol that controls the minimum reflux ratio. Therefore, the overall energy requirement to produce anhydrous ethanol can be reduced by combining fractional distillation up to 92–94 wt.% ethanol or less with one of the several processes discussed above for the production of anhydrous ethanol.

An energy-efficient fractional distillation scheme consumes energy of 4.8–7.0 GJ/m^3 of anhydrous ethanol. Since the various dehydration methods consume different amount of energy, there is a possibility of minimizing energy requirement for producing anhydrous ethanol. Black [26] compared six conventional processes (vacuum distillation, azeotropic distillation with benzene, pentane, diethyl ether, extractive distillation with ethylene glycol, gasoline) and showed that the energy consumption lies between 31% and 64% of the heating value of anhydrous ethanol (The combustion energy of anhydrous ethanol is reported as 21.8–23.5 GJ/m^3 of anhydrous ethanol). This means a range of about 9.21–18.84 MJ/kg of anhydrous ethanol. Vacuum distillation process consumes 11.72 MJ/kg of anhydrous ethanol. Azeotropic distillation process consumes 10.05–15.49 MJ/kg of anhydrous ethanol. Extractive distillation with gasoline and ethylene glycol consumes 9.21–18.84 MJ/kg of anhydrous ethanol. Ligero and Ravagnani [74] computed the energy requirement of extractive distillation with potassium acetate to be 9.27 MJ/kg of anhydrous ethanol. Barba et al. [68] assessed the energy requirement of extractive distillation with calcium chloride to be 5.02 MJ/kg of anhydrous ethanol. About 10% of this energy is required to eliminate the crystallization water in order to obtain anhydrous calcium chloride to be recycled. It was found that extractive distillation using calcium chloride [57,63] has a lower energy requirement as compared with all the conventional alternatives (and solvent extraction, as well) and almost the same consumption as membrane pervaporation (which, at present, is widely used to produce ethanol for gasohol in some of the northcentral corn-producing states of USA).

The non-distillation processes for the production of anhydrous ethanol include solvent extraction, adsorption and membrane pervaporation. Solvent extraction process requires 6.28 MJ/kg of anhydrous ethanol. The heat given off during adsorption is stored by adsorbent. The overall energy required by corn meal adsorbent is 170 kJ/kg of anhydrous ethanol. Starting from a liquid feed of 92 wt.% ethanol at ambient temperature. This includes the energy required to heat the feed from ambient and vaporize it, the energy needed to heat the regenerating air from ambient to an inlet temperature of 95 °C and heat losses from the overall system. The heat of adsorption is retained in the bed if adsorption is stopped when the concentration wave begins to leave the adsorption column. Hence it is desirable to adsorb upflow and regenerate by

Table 4
Energy consumption of various processes for anhydrous ethanol production [26,57,63,68,74].

Type of process	Energy consumption (MJ/kg ethanol)	Fraction of ethanol heating value	Range of concentration (wt.%)
Distillation processes			
Low pressure distillation	11.72	40	6.4–98
Azeotropic distillation			
Pentane	10.05	34	6.4–99.95
Benzene	15.49	38	6.4–99.95
Diethyl ether	12.56	43	6.4–99.95
Extractive distillation			
Gasoline	9.21	31	6.4–99.95
Ethylene glycol	18.84	64	6.4–99.95
Extractive distillation with salt			
Calcium chloride	5.02	17	7.5–99
Potassium acetate	9.27	31	60
Non-distillation processes			
Solvent extraction	6.28	21	10–98
Pervaporation	4.61	16	8–99.5

passing gas downflow, thus making use of some of the heat of adsorption stored at the upper part of the bed to drive off adsorbed water from the bottom of the bed. The energy required to regenerate the adsorption is less than 528 kJ/kg of anhydrous ethanol obtained from ethanol vapor containing 7.4% water. Kaminski et al. [92] compared vapor permeation, pervaporation, azeotropic distillation and adsorption on molecular sieve processes on the basis of cost of production of anhydrous ethanol. For small installations (100 dm^3/day) they showed the cost of ethanol dehydration by azeotropic distillation is twice as high and in the case of adsorption 1.5 times higher than that in pervaporation. Table 4 lists a number of separation routes and also shows the energy necessary to accomplish the water removal from aqueous ethanol.

4. Conclusions

Anhydrous ethanol is one of the biofuels produced today and it is a subset of renewable energy. It is considered to be an excellent alternative clean-burning fuel to gasoline. Any biological material that has sugar, starch or cellulose can be used as biomass for producing anhydrous ethanol. There are several sources of these biological materials, such as molasses, corn, bagasse. Since ethanol–water solution forms a minimum-boiling azeotrope of composition of 89.4 mol% ethanol and 10.6 mol% water at 78.2 °C and standard atmospheric pressure, the production of anhydrous ethanol from dilute ethanol–water solutions produced by fermentation process involves fractional distillation up to 92–94 wt.% ethanol or less followed by one of the several dehydration processes such as chemical dehydration process, dehydration by vacuum distillation process, azeotropic distillation process, extractive distillation processes, membrane processes, adsorption processes, diffusion distillation process. These dehydration processes of manufacturing anhydrous ethanol have been improved continuously due to the increasingly strict requirements for quantity and quality of this product. These processes are described and compared on the basis of energy requirements which vary in the range of 16–64% of ethanol heating value.

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